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EP 0056409



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ³: D21C 3/20	A1	(11) International Publication Number: WO 82/00483 (43) International Publication Date: 18 February 1982 (18.02.82)
(21) International Application Number: PCT/EP81/00105 (22) International Filing Date: 24 July 1981 (24.07.81) (31) Priority Application Number: 359443 (32) Priority Date: 25 July 1980 (25.07.80) (33) Priority Country: CA (71) Applicant: BAU- UND FORSCHUNGSGESELLSCHAFT THERMOFORM AG [CH/CH]; Ryfstrasse 50, CH-Murten/Fribourg (CH). (72) Inventors: PASZNER, Laszlo; 3906 West 33rd Avenue, Vancouver, British Columbia (CA). CHANG, Pei-Ching; 180 West 22nd Avenue, Vancouver, British Columbia (CA). (74) Agent: HANSMANN, Axel; Albert-Rosshaupter-Str. 65, D-8000 München 70 (DE).		(81) Designated States: AT (European patent), BR, DE (European patent), FI, FR (European patent), JP, SE (European patent), SU. Published <i>With international search report</i>
(54) Title: PULPING OF LIGNOCELLULOSE WITH AQUEOUS ALCOHOL AND ALKALINE EARTH METAL SALT CATALYST (57) Abstract A high yield of a high quality pulp is obtained by cooking fragmented lignocellulose material at a temperature of 180 to 240°C with a mixture of methanol or ethanol and water containing 80 to 98 percent by volume of the alcohol, the mixture containing dissolved from 0.001 to 0.5 molar of an alkaline earth metal salt, and from zero to 0.005 normal/molar of (a) a strong mineral acid, or (b) a weak mineral acid or (c) a weak organic acid or (d) an acid reacting metal salt to aid rapid delignification. In addition, optionally, pressures substantially higher than developed in enclosed spaces by the vapors of the solvent mixture at the cooking temperature are used to further increase the delignification rate and suppressing carbohydrate degradation. Lignin is obtained in powder form by low temperature evaporation of the alcohol from the spent cooking liquor.		

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5 PULPING OF LIGNOCELLULOSE WITH AQUEOUS ALCOHOL
AND ALKALINE EARTH METAL SALT CATALYST

10 The invention relates to a method for the digestion
of lignocellulose material which comprises cooking
the fragmented lignocellulose material with an
aqueous methyl or ethyl alcohol containing dissolved
therein an alkaline earth metal salt, namely a
15 chloride or nitrate of magnesium, calcium or barium
or magnesium sulfate or a soluble mixture thereof in
a concentration of less than 1.0 molar and, op-
tionally, an acid reacting substance in a concentra-
tion of less than 0.008 normal for not more than two
20 hours at a temperature above 130°C, the amount of
cooking liquor being at least 4 parts by weight per
part by weight of the lignocellulose material, re-
covering the fibres liberated thereby from the
cooking liquor, and separating the remaining spent
25 cooking liquor into solvent, lignin and sugars.

Such a process is described in German Offenlegungs-
schrift No. 29.20 731. The main advantages of this
known process over the conventional organosolv pul-
30 ping processes which use mixtures of alcohol and
water as the cooking liquor without the addition of
an alkaline earth metal salt are the much more rapid
delignification rate and the recovery of the lignin
in powder form rather than as a dark-brown quasi-
35 molten phase which is not easy to remove from the
equipment and is of low commercial value.

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5 The problem to be solved by the invention is to
improve delignification specificity for all ligno-
cellulose species and thereby to increase the yield
of cellulose pulp, to reduce viscosity losses in
10 cellulose due to carbohydrate degradation, improve
the quality and stability of dissolved lignin in
solution and increase the uniformity of digestion
at reduced cooking times of air-dry softwood chips
and increase temperature stability of lignocellulose
materials during high temperature digestion.

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These problems are solved by the method as claimed.

Great Britain patent No. 357 821 (Kleinert)
describes a process for the decomposition of vege-
20 table fibrous matter for the purpose of obtaining
the cellulose and the incrusting materials which
uses as the decomposing agent mixtures of alcohol
and water with a water content of 20 to 75 percent
by weight and states on page 1, lines 74 to 77, that
25 with 96 percent alcohol a dark brown residue amount-
ing to 92 percent of the raw material is obtained.
An article by Theodor Kleinert in "Zeitschrift f.
angewandte Chemie" 44 (1931), pages 788 to 791,
states on page 789 that absolute alcohol solves only
30 little lignin and nearly no carbohydrates, and on
same page, lines 4 to 2 from the bottom with
reference to figure 1 that maximum digestion results
with an alcohol content of 45 to 50 percent, and
United States patent No. 3 585 104 (Kleinert) states
35 in lines 42 to 44 of c.2 that methanol or ethanol in
the medium concentration range between about 20 per-

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5 cent and 75 percent by weight alcohol content have a stronger delignifying effect upon fibrous plant materials than the water-free alcohols.

10 Therefore it was surprising that by the use of an aqueous methanol or ethanol of between 80 and 98 percent by volume of the alcohol in the presence of the alkaline earth metal salts and, optionally, the acid substances specified in the claims much better results can be obtained than with the use of the
15 lower range of alcohol contents of the cooking liquor.

20 It was also surprising that if in addition to the alkaline earth metal salts one or more of the specified acid reacting substances are added to the cooking liquor the effect of the additive is much greater than with the addition of either the alkaline earth metal salt or the acid reacting substances, so that the total amount of additives can be substan-
25 tially reduced.

30 In the course of the digestion of the lignocellulose material organic acids such as formic or acetic acids are generated. These acids should be taken into account when defining the amount of acidic substance to be added to the cooking liquor, so that the pH of the reaction mixture be maintained preferably above 3.8 and below 7.0 regardless of the amount of added or autocatalytically generated acids. Such pH control
35 is easily achieved by mild buffering of alkali metal ion systems such as occurs with technical grades

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5 of the alkali earth metal salts used in this inven-
tion or as afforded by standard buffering salts
specified for this pH range. It is further a very
important characteristic of such systems that the
actual cooking pH changes only within relatively
10 narrow limits between 3.8 to 5.6 or not at all
depending on the wood species acidity and the degree
of buffering produced by the alkali metal ions pre-
sent or added to the cooking liquor.

15 In the process of the invention methanol is the
preferred alcohol, but where methanol is not
available in sufficient amount ethanol can be used
as well. The preferred alcohol content of the
cooking liquor is 80 to 98 percent by volume, but
20 the higher percentages within this range are rela-
tively difficult to achieve because of the moisture
contained in the lignocellulose starting material.

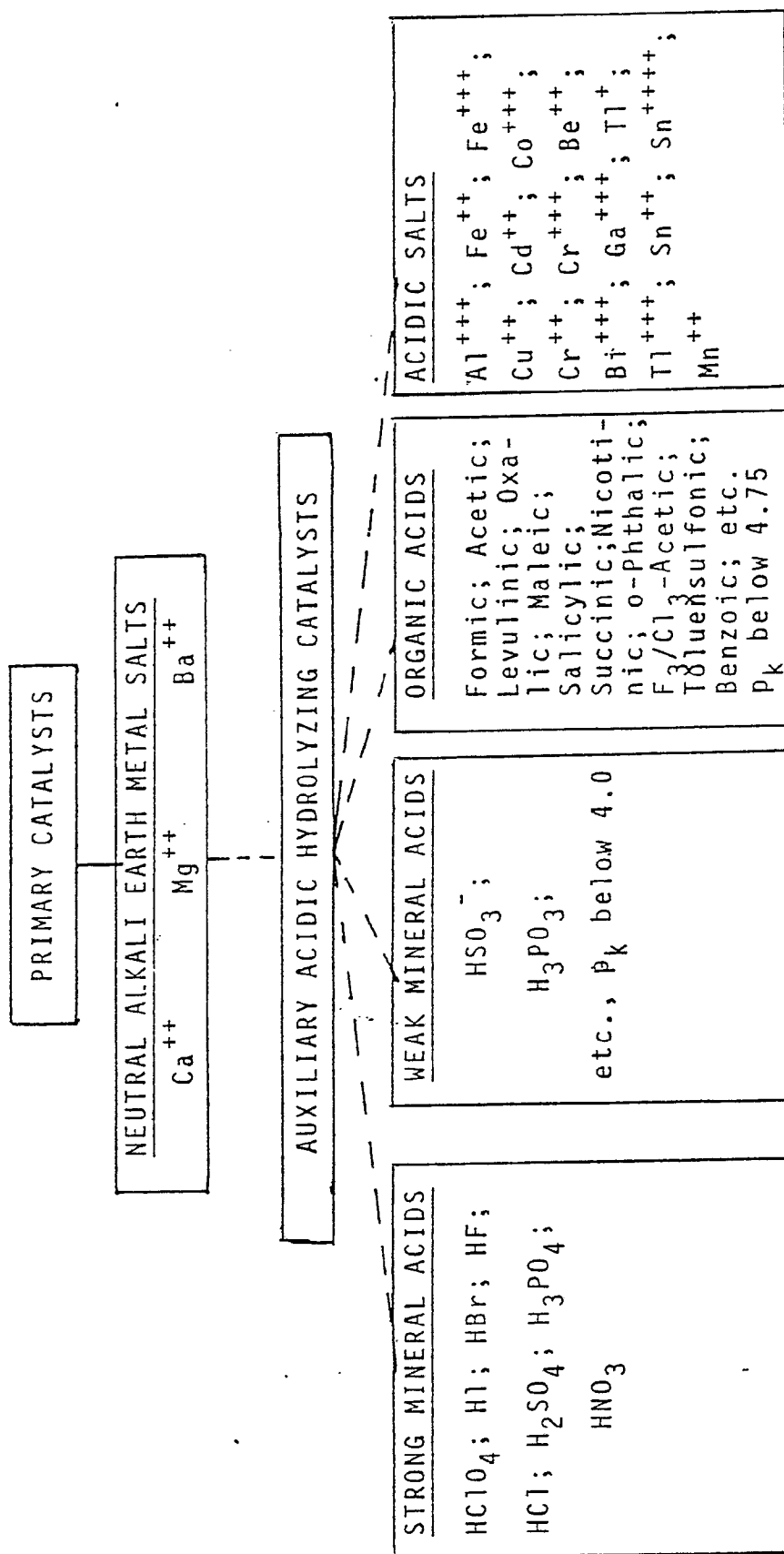
25 The preferred ratio of lignocellulose material to
cooking liquor is 1:6 to 1:20.

At the high alcohol-water ratios and with the addi-
tives claimed not only delignification is more com-
plete, but carbohydrate degradation is suppressed,
30 especially if also excess pressure of more than 5
bars over that developed by the vapors of the
cooking liquor at the temperature used is applied.

35 The following table 1 shows the combinations of
alkaline earth metal and acidic hydrolyzing sub-
stances which may be used in the process of the
invention:

TABLE 1

POSSIBLE COMBINATIONS OF PRIMARY AND AUXILIARY ACIDIC HYDROLYZING CATALYSTS



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EXAMPLE I

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To investigate the effectiveness of delignification specificity and yield of fibre attainable when using the novel largely methanol-water solvent extraction in the presence of alkali earth metal salts and auxiliary acid catalysts a number of cooks were carried out in laboratory-scale stainless steel pressure vessels having internal dimensions of 11 cm height and 4.5 cm diameter.

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Wood chips in both air-dry and green conditions were conditioned to a uniform moisture content before the pulping trials. Batch quantities of commercial size chips were charged into the digester with ten times their weight of cooking liquor containing predetermined quantities of the salt catalysts. The volume ratio of methanol to water ranged between 90:10. The sealed stationary vessel was quickly brought to cooking temperature in a thermostatically controlled glycerine bath and the temperature held constant for the cooking interval required. The reported cooks are those which at the end of the stated period produced a free pulp when slurried in a disintegrator at slow stirred speed.

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At the end of each cook the digester was rapidly cooled with cold water and the liquor decanted. After disintegration of the cooked chips in acetone or cooking solvent and final washing in water the pulp was air-dried to constant weight and yield, and Kappa number and TAPPI 0.5 per cent viscosity determined in an effort to characterize the pulp. The results are summarized in TABLE 2.

TABLE 2

COOKING SPRUCE WOOD WITH PRIMARY AND AUXILIARY
ACID HYDROLYZING CATALYSTS

	C A T A L Y S T 1° normal/molar	2°	Cooking Time* min	Cooking Temp. °C	Pulp Yield %	Kappa No.	TAPPI 0.5% Viscosity Pa·s ⁻³
10	H ₂ SO ₄ 0.0038		40	200	46	39	3.7
15		MgCl ₂ 0.01	50	200	No fibre separation		
	H ₂ SO ₄ 0.001	MgCl ₂ 0.0038	35	200	58	38	19
20		CaCl ₂ 0.01 ²	45	200	No fibre separation		
	SnCl ₂ 0.0002	CaCl ₂ 0.01 ²	55 40	200 200	63 58	77 67	22 24
25	AlCl ₃ 0.003		70	200	No fibre separation		
	AlCl ₃ 0.0003	CaCl ₂ 0.01 ²	40	200	60	67	24
	H ₂ SO ₃ 0.003		70	200	No fibre separation		
	H ₂ SO ₃ 0.003	CaCl ₂ 0.003	65	200	67	93	22
30	HCl 0.0025		40	200	No fibre separation		
	HCl 0.002	CaCl ₂ 0.025	45	200	59	56	27

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TABLE 2 - ContinuationCOOKING SPRUCE WOOD WITH PRIMARY AND AUXILIARY
ACID HYDROLYZING CATALYSTS

10	C A T A L Y S T		Cooking	Cooking	Pulp	Kappa	TAPPI 0.5%
	1°	1°	Time*	Temp.	Yield	No.	Viscosity
	normal/molar		min	°C	%		Pa·s ⁻³
	Salicy- lic Acid						
	0.005		70	200	No fibre separation		
15	Salicy- lic Aid	MgCl ₂					
	0.0001	0.005	55	200	62	60	28
	Oxalic Acid						
	0.005		70	200	No fibre separation		
20	Oxalic	CaCl ₂					
	Acid		65	200	61	78	27
			85	200	58	67	26
	0.0001	0.005	55	210	63	57	30
	Acetic Acid						
	0.005		70	200	No fibre separation		
25	Acetic	CaCl ₂					
	Acid		55	200	61	68	34
	0.0001	0.005					

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* Includes 11 min heating-up time to temperature

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5 The data of TABLE 2 show in particular that effective
delignification selectivity and fibre liberation is
obtained at alkali earth metal salt and auxiliary
acid catalyst concentrations normally ineffective
10 under the conditions indicated in TABLE 2. The
synergistic additive effect of the two types of cata-
lysts is the more surprising especially in cases
where the combined amounts of both catalysts remains
substantially below that determined earlier as the
minimum effective salt concentration required to
15 attain fibre liberation.

In TABLE 3 the effect of varying alcohol-water
ratios and the compensating effect of increased tem-
perature and prolonged cooking time are demonstrated
20 on spruce wood. Pulping aspen and spruce wood at the
high alcohol concentrations indicated in TABLE 3
shows that in the presence of 0.05 molar salt concen-
trations, with or without the secondary acid cata-
lysts, free fibre separation is obtained within 15
25 to 60 min (including 11 minutes as heating-up time)
and in spite of the relatively high Kappa number,
fibre liberation was obtained at relatively high pulp
yield. The pulps had viscosities between 20 to 52
Pa.s⁻³ corresponding to a degree of polymeriza-
30 tion of 1320 to 2200 (Rydholm, Pulping Processes,
page 1120).

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TABLE 3

VARIATION OF METHANOL-WATER RATIO, COOKING TEMPERATURE, AND TIME IN CaCl_2 -CATALYZED (0.05 MOLES PER L) PULPING OF ASPEN AND SPRUCE WOODS

	Species	Alcohol to Water Ratio*	C O O K I N G Temp. °C	Time** min.	P U L P		TAPPI 0.05% CuEn Viscosity, ⁻³ Pa·s
					Yield %	Kappa No.	
10	Aspen Wood	70:30	190	30	61	25	24
		80:20	190	42	61	14	32
		90:10	190	35	64	20	50
		90:10	190	50	63	15	38
		95: 5	190	30	67	39	44
		Anhydr.	190	50	69	37	42
		90:10	200	10	61	19	36
		95: 5	220	8.5	66	33	40
15	Aspen Wood	70:30	190	30	61	25	24
		80:20	190	42	61	14	32
		90:10	190	35	64	20	50
		90:10	190	50	63	15	38
		95: 5	190	30	67	39	44
		Anhydr.	190	50	69	37	42
		90:10	200	10	61	19	36
		95: 5	220	8.5	66	33	40
20	Spruce Wood	70:30	200	30	56	47	23
		80:20	200	50	59	45	-
		80:20	210	13	70	95	46
		80:20	210	25	60	42	37
		90:10	210	20	75	86	48
		90:10	210	25	69	70	-
		90:10	220	11	78	112	-
		90:10	220	13	74	99	-
25	Spruce Wood	90:10	220	20	61	59	40
		90:10	220	25	59	39	43
		95: 5	200	50	66	75	46
		95: 5	200	55	63	59	-
		95: 5	210	30	67	73	52
		95: 5	220	15	66	60	48
		95: 5	220	25	60	51	42
		98: 2	220	35	63	52	35
30	Spruce Wood	90:10	220	20	61	59	40
		90:10	220	25	59	39	43

* Wood/Liquor ratio 1:10

** Cooking time includes 11 minute heating-up time

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5 It can be observed that the system behaves according
the laws of Arrhenius with respect to temperature in
that cooking times to fibre separation and compar-
able Kappa number decrease with increasing tempera-
10 ture even for the unconventionally high cooking tem-
perature of 220°C while viscosity is little or not
at all affected even at this high temperature in the
presence of 80 percent or higher alcohol volume in
the cooking liquor the parameter most affected is
15 residual lignin with only minor losses in pulp yield.
An accelerated carbohydrate degradation is observed
with alcohol:water ratios of 70:30 and lower, the
carbohydrate stabilizing effect of high alcohol con-
tent of the digestion mixture is thus a truly sur-
prising effect quite contrary to tendencies reported
20 in the prior art. High alcohol content liquors fur-
ther allow more thorough delignification within a
given digestion time. The table indicates that a pulp
yield in excess of 60 percent can be had from cooking
spruce wood at a Kappa number of 45 and below a
25 cooking time of 25 (minus 11) minutes.

The process also appears to be quite tolerant to ex-
tended cooking times wherein the parameter most
affected is residual lignin content.

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In a number of cooks (not reported) wherein the
cooking time was not sufficient to allow fibre sepa-
ration, the chips were found to be sufficiently soft
so that a semi-mechanical pulp could be prepared on
35 treatment at high speed in a blender. In certain of
the cooks where "No fibre separation" (NFS) was

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5 reported earlier after a predetermined cooking time
it was found that, on high-speed blending acceptable
pulp could be produced. It is therefore to be under-
stood that this invention is not limited to the
length of cooking at which a free fibre state is
10 reached but also includes cooks for only a sufficient
time at which minimal delignification and hemicellu-
lose removal took place to produce a semi-chemical
pulp product of ultra high yields say about 80 to 90
percent. Fully defiberized pulps can be had at 75
15 percent pulp yield.

The pulping liquor when subjected to vacuum distilla-
tion at low temperature yields a flocculated lignin
precipitate. After recovery of the lignin by filtra-
20 tion or centrifuging a sugar solution having a solids
concentration up to 25 percent is obtained. Charcoal
filtration removes most of the yellow color due to
the water soluble lignin depolymerisation products.
The molecular weight distribution of the lignin
25 shows one major and 2 to 3 minor peaks with the
maximum being under 3800. Purification of the crude
lignin is most effectively done by redissolution in
acetone and spray drying in vacuum at low temperature
to avoid melting and resinification. A dried solid
30 filter cake is easily broken up into a free flowing
tan-colored powder.

In conjunction with these tests summative carbo-
hydrate analyses were also carried out for the ori-
35 ginal wood of spruce and aspen poplar and the pulps
prepared therefrom. Findings of these investigations

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are summarized in TABLE 4. Sugar compositions of alpha-celluloses are those prepared from the pulps. The aspen pulp samples were found to be rich in xylan and spruce pulp samples rich in mannan with the other less important hemicelluloses being present in smaller amounts. Retention of these hemicelluloses explain the improvements in higher than usual yield had earlier with this process.

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TABLE 4
SUGAR ANALYSES OF ASPEN AND SPRUCE WOOD, PULP AND ALPHA-CELLULOSE

SPECIES	SAMPLE	SUGAR CONCENTRATION, %			
		GLUCOSE	XYLOSE	MANNOSE	GALACTOSE ARABINOSE
A S P E N	Holocellulose	57.9	16.0	3.4	1.5 0.2
	Pulp *	82	13.1	3.0	Trace Trace
	Alpha-Cellulose	97 (80)**	1.0	1.0	Trace Trace
S P R U C E	Holocellulose	49.9	6.0	11.9	2.6 1.1
	Pulp ***	76	4.8	10.7	Trace Trace
	Alpha-Cellulose	97 (87)**	0.5	2.3	Trace Trace

* 2.0% residual lignin

** denotes proportion of glucan originally present in wood

*** 8.5% residual lignin

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5 Analysis of the sugar wort showed (data not reported
herewith) that the majority of dissolved sugars was
present as monomers (about 30 to 50%) and the rest
as low molecular-weight oligomers. Surprisingly no
10 furfurals were detected in the residual liquors
following the cooks done with the alkali earth metal
salts as primary catalysts alone. In prior acid
catalysed organosolv cooking degradation (dehydra-
tion) of the xylose and hexose sugars to furfurals
is a simultaneous reaction with hydrolysis and de-
15 lignification and was found to be prevalent at the
higher temperatures (above 200°C). In solution these
furfurals are very active and condense readily with
the dislodged low molecular-weight lignin fragments
to form alcohol insoluble products. The absence of
20 furfurals in residual liquors of this invention
assures complete solubility of the dissolved lignin
and a high degree of sugar recovery as by-product.
The sugar solutions are readily fermentable into
ethanol, yeast and other fermentation products. The
25 alkali earth metal catalysts do not interfere with
such fermentation processes and can also be safely
discharged in mill effluents.

30 Very similar results were obtained with other ligno-
cellulose species. Sugarcane rind behaved like aspen
poplar, jack pine, ponderosa pine and Western hem-
lock; and Douglas-fir behaved like spruce wood
whereas birch and Eucalyptus species proved to be
intermediate species and wheat straw was found to
35 be a more difficult species than spruce requiring
larger catalyst concentrations than spruce to yield

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5 pulps with equal degree of delignification. Numerous
other secondary catalysts listed in TABLE 1 were also
tested but their results not reported herein due to
the large similarity in results obtainable on apply-
ing them. In these cases some adjustments in cooking
10 conditions were necessary to compensate for the
variation in acid strength.

EXAMPLE II

15 While the examples given before show quite adequate
selectivity for delignification at thermodynamically
defined conditions, allowing or causing an increase
in internal pressures higher than those normally
found for enclosed liquids under free expansion con-
ditions, or by deliberate application of pressure
20 from a pressure intensifier or through compressed
inert gases was found to influence the delignifica-
tion and carbohydrate degradation rates at especi-
ally high alcohol water ratios and high temperatures
by shifting the rate constant in a very favourable
25 manner. In general it was observed, that in order to
achieve the same degree of delignification at high
alcohol water ratios especially over 85:15, higher
temperatures were required. Thus the desired deligni-
fication rates could be maintained and cooking times
30 could be held within reasonable limits. It was also
found that as the system pressure increased so did
the pulp viscosity, indicating the beneficial effects
of pressure on delignification rates and on lowering
the sensitivity of the carbohydrates to increased
35 thermal treatment which normally led to lower visco-
sities. It was also observed that the pressure

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5 effects were not linked to increased penetration
into the wood matrix since when air-dry spruce chips
were cooked with 90:10 or 95:5 alcohol:water solvent
mixtures in the presence of 0.05 moles of CaCl_2 at
210°C under normal autogeneous pressure (35 atm and
10 39 atm, respectively) complete penetration of the
chips is observed within the first 10 minutes of
cooking yet poor fibre separation occurs even after
prolonged cooking, up to 50 minutes. Under the same
conditions but with added or internally generated
15 overpressure fully cooked chips are obtained which
show the same fibre liberation tendencies as chips
cooked at lower alcohol concentration (under 80:20).
While this in itself was a surprising effect, ana-
lysis of the resulting pulps showed a consistently
20 higher pulp viscosity. In fact the pulp viscosity
consistently increased with the level of pressure
applied or generated. Some data on high pressure
cooks are reproduced in TABLE 5. In comparison the
previous test data provided in TABLE 5 wherein the
25 increased selectivity of delignification and the
lower carbohydrate degradation (higher pulp viscosi-
ty) and a significant reduction in cooking time with
increased pressure is clearly evident. Thus the con-
founded effect of high alcohol concentration and high
30 pressure is an important aspect of this invention in
that it allows faster delignification of any wood
species to low residual lignin content levels which
earlier were not possible without considerable losses
in cellulose viscosity. The pressure effect dimini-
35 shes somewhat when solvent compositions lower than
80:20 alcohol:water content are used.

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TABLE 5

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EFFECT OF INCREASED PRESSURE ON DELIGNIFICATION
RATES AND CARBOHYDRATE DEGRADATION AT VARIOUS
ALCOHOL:WATER RATIOS ON COOKING SPRUCE WOOD

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Liquor Comp.*	C o o k i n g Temp. °C	Pres- sure bar	Time min	Yield %	Kappa No.	TAPPI 0.5% Viscosity Pa·s ⁻³
80:20	210	285	25	60	41	57
80:20	210	285	30	57	45	47
80:20	210	285	35	52	27	26
80:20	210	33	25	61	63	55
80:20	210	33	30	59	56	40
80:20	210	33	35	57	45	38
90:10	210	320	20	75	86	62
90:10	210	320	25	69	71	50
90:10	210	320	35	63	62	43
90:10	210	320	60	57	36	41
90:10	210	40	35	59	100	24
90:10	210	40	80	52	100	10

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5 All cooks were done at a wood:liquor ratio of 1:10.
Cooking times include 9 minutes for heating-up to
temperature. In a similar series of cooks with 90:10
alcohol:water mixture, cooked at 210°C and 320 bar it
10 was established that the ratio of lignin to carbo-
hydrate removed can be as high as 9.48 on spruce
wood and delignification could be persued to a Kappa
number of 14.5 at a residual pulp yield of 49%. The
viscosity dropped from an initial value of $55 \text{ Pa}\cdot\text{s}^{-3}$ to
15 24 on cooking for 50 minutes under the above con-
ditions. Thus the pulp properties generally increase
with increased overpressure at the lower temperatures
possible. Interestingly, the alpha-cellulose yield
of the highly delignified pulp was still 43.2% based
on wood as 100, representing 88% of the total pulp
20 mass. All pulps produced under these conditions were
fully defiberized and produced no rejects on scree-
ning through a No. 6-cut standard laboratory flat
pulp screen.

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CLAIMS

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1. A method for the digestion of lignocellulose material which comprises cooking the fragmented lignocellulose material with an aqueous methyl or ethyl alcohol containing dissolved an alkaline earth metal salt, namely a chloride or nitrate of magnesium, calcium or barium or magnesium sulfate or a soluble mixture thereof in an amount of less than 1.0 molar, and optionally an acid reacting substance in an amount of less than 0.008 normal for not more than two hours at a temperature above 130°C, the amount of cooking liquor being at least 4 parts by weight per part by weight of the lignocellulose material, recovering the fibres liberated thereby from the cooking liquor, and separating the remaining spent cooking liquor into solvent, lignin and sugars, characterized in that as the cooking liquor an aqueous methanol or ethanol of between 80 and 98 percent by volume of the alcohol and containing the alkaline earth metal salt in a concentration of from 0.001 to 0.5 molar and the acid reacting substance in a concentration of from zero to 0.005 normal is used, and in that the acid reacting substance is a strong mineral acid, a weak mineral acid, an organic acid or an acid reacting salt.

2. A method according to claim 1, characterized in that the cooking temperature is maintained at 170 to 240°C.

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3. A method according to claim 1, characterized in that a cooking liquor is used which contain from zero to 0.001 normal of hydrochloric, sulfuric, nitric or phosphoric acid as the strong mineral acid.

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4. A method according to claim 1, characterized in that a cooking liquor is used which contains from zero to 0.005 normal of sulphurous, phosphorous or boric acid as the weak mineral acid.

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5. A method according to claim 1, characterized in that a cooking liquor is used which contains from zero to normal of formic, acetic, oxalic, salicylic, maleic, l-malic, succinic, o-phthalic or benzoic acid as the organic acid.

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6. A method according to claim 1, characterized in that a cooking liquor is used which contains from zero to 0.0025 molar of SnCl_4 , AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, FeCl_2 or FeCl_3 as the acid reacting salt.

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7. A process according to one of the preceding claims, characterized by the fact, that the pressure during the cook is maintained at least five bars higher than that developed by the vapors of the cooking liquor at the cooking temperature.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 81/00105

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. ³ : D 21 C 3/20																	
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 5px;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Classification System </td> <td style="width: 50%; border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding-top: 10px;">Int.Cl.³:</td> <td style="border: none; padding-top: 10px;">D 21 C 3/20</td> </tr> </table> <div style="text-align: center; margin-top: 10px; font-size: small;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵</div>			Classification System	Classification Symbols	Int.Cl. ³ :	D 21 C 3/20											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; text-align: left; padding: 5px;">Category *</th> <th style="width: 70%; text-align: left; padding: 5px;">Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 20%; text-align: left; padding: 5px;">Relevant to Claim No. ¹⁵</th> </tr> </thead> <tbody> <tr> <td style="padding: 5px;"></td> <td style="padding: 5px;">DE, A, 2920731, published 29th May 1980, see the whole document, Bau- und Forschungsgesellschaft Thermoform cited in the application --</td> <td style="padding: 5px; text-align: center;">1-3</td> </tr> <tr> <td style="padding: 5px;"></td> <td style="padding: 5px;">US, A, 2560638, published 17th July 1951, see column 1, lines 1-3, 30-38; column 2, lines 27-50; examples 1,2, H. Dreyfus --</td> <td style="padding: 5px; text-align: center;">1,3</td> </tr> <tr> <td style="padding: 5px;"></td> <td style="padding: 5px;">US, A, 2022654, published 3rd December 1935, see the whole document, H. Dreyfus --</td> <td style="padding: 5px; text-align: center;">1-3,7</td> </tr> <tr> <td style="padding: 5px;"></td> <td style="padding: 5px;">CH, A, 386823, published 30th April 1965, see the whole document, Ceskoslovenska Akademie Ved. -----</td> <td style="padding: 5px; text-align: center;">1,4</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁵		DE, A, 2920731, published 29th May 1980, see the whole document, Bau- und Forschungsgesellschaft Thermoform cited in the application --	1-3		US, A, 2560638, published 17th July 1951, see column 1, lines 1-3, 30-38; column 2, lines 27-50; examples 1,2, H. Dreyfus --	1,3		US, A, 2022654, published 3rd December 1935, see the whole document, H. Dreyfus --	1-3,7		CH, A, 386823, published 30th April 1965, see the whole document, Ceskoslovenska Akademie Ved. -----	1,4
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<div style="font-size: x-small;"> * Special categories of cited documents: ¹⁸ <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> "A" document defining the general state of the art "E" earlier document but published on or after the international filing date "L" document cited for special reason other than those referred to in the other categories "O" document referring to an oral disclosure, use, exhibition or other means </div> <div style="width: 48%;"> "P" document published prior to the international filing date but on or after the priority date claimed "T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention "X" document of particular relevance </div> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> Date of the Actual Completion of the International Search ¹ <div style="text-align: center; margin-top: 10px; font-size: large;">26th October 1981</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> Date of Mailing of this International Search Report ² <div style="text-align: center; margin-top: 10px; font-size: large;">10th November 1981</div> </td> </tr> <tr> <td style="border: none; vertical-align: top;"> International Searching Authority ¹ EUROPEAN PATENT OFFICE Branch at The Hague P.O.Box 5818 Patentlaan, 2 2280 HV RIJSWIJK (ZH) The Netherlands </td> <td style="border: none; vertical-align: top;"> Signature of Authorized Officer ¹⁹ <div style="text-align: center; margin-top: 10px;"> G.L.M. Kruidenberg </div> </td> </tr> </table>			Date of the Actual Completion of the International Search ¹ <div style="text-align: center; margin-top: 10px; font-size: large;">26th October 1981</div>	Date of Mailing of this International Search Report ² <div style="text-align: center; margin-top: 10px; font-size: large;">10th November 1981</div>	International Searching Authority ¹ EUROPEAN PATENT OFFICE Branch at The Hague P.O.Box 5818 Patentlaan, 2 2280 HV RIJSWIJK (ZH) The Netherlands	Signature of Authorized Officer ¹⁹ <div style="text-align: center; margin-top: 10px;"> G.L.M. Kruidenberg </div>											
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